

# Adsorption and Photocatalytic Degradation of Methylene Blue on TiO<sub>2</sub> Thin Films Impregnated with Anderson-Evans Al-Polyoxometalates: Experimental and DFT Study

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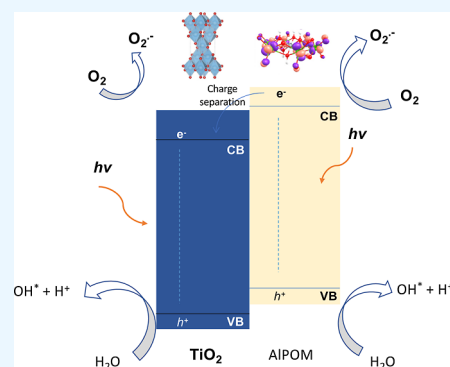
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**ABSTRACT:** In this work, we fabricated a TiO<sub>2</sub> thin film, and the same film was modified with an Anderson aluminum polyoxometalate (TiO<sub>2</sub>-ALPOM). Physical–chemical characterization of the catalysts showed a significant change in morphological and optical properties of the TiO<sub>2</sub> thin films after surface modification. We applied the kinetic and isothermal models to the methylene blue (MB) adsorption process on both catalysts. The pseudo-second order model was the best fitting model for the kinetic results;  $q_e$  (mg/g) was 11.9 for TiO<sub>2</sub> thin films and 14.6 for TiO<sub>2</sub>-ALPOM thin films, and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) was  $16.3 \times 10^{-2}$  for TiO<sub>2</sub> thin films and  $28.2 \times 10^{-2}$  for TiO<sub>2</sub>-ALPOM thin films. Furthermore, the Freundlich model was suitable to describe the isothermal behavior of TiO<sub>2</sub>,  $K_F$  (5.42 mg/g), and  $1/n$  (0.312). The kinetics of photocatalytic degradation was fitted using the Langmuir–Hinshelwood model;  $k_{ap}$  was  $7 \times 10^{-4}$  min<sup>-1</sup> for TiO<sub>2</sub> and  $13 \times 10^{-4}$  min<sup>-1</sup> for TiO<sub>2</sub>-ALPOM. The comparative study showed that TiO<sub>2</sub> thin films reach a 19.6% MB degradation under UV irradiation and 9.1% MB adsorption, while the TiO<sub>2</sub>-ALPOM thin films reach a 32.6% MB degradation and 12.2% MB adsorption on their surface. The surface modification improves the morphological, optical, and photocatalytic properties of the thin films. Finally, the DFT study supports all the previously shown results.



## 1. INTRODUCTION

In the last few decades, the emerging pollutants have become a relevant issue, as they can affect the environmental quality and the public health.<sup>1</sup> They represent a wide variety of chemical compounds [e.g., pharmaceuticals, hormones and steroids, disinfection by-products, hygiene and personal care products, surfactants, flame retardants, industrial compounds, agrochemicals (pesticides, fertilizers, and growth agents), microplastics, and dyes].<sup>2,3</sup> These compounds are chemically and physically stable enough to withstand conventional treatment processes and are not properly degraded in treatment plants.<sup>4</sup> Heterogeneous photocatalysis (HP) has demonstrated its potential for treatment of various emerging pollutants.<sup>5,6</sup> HP can convert solar energy into chemical energy under the action of photocatalysts; this technique provides new ideas for the development of traditional catalysis. Nowadays, titanium dioxide (TiO<sub>2</sub>) has become the main photocatalyst that is studied for the development of environmental applications.<sup>7,8</sup> However, TiO<sub>2</sub> has two drawbacks: (i) high band gap energy value (3.2 eV, active only under UV irradiation) and (ii) low quantum efficiency in charge-carrier generation.<sup>9</sup> Various methods have been reported to solve these issues [e.g., metal doping,<sup>10</sup> quantum dots,<sup>11</sup> sensitization with a smaller band gap semiconductors,<sup>12</sup> surface plasmon resonance,<sup>13</sup> sensitization with natural and synthetic dyes,<sup>14,15</sup> and surface

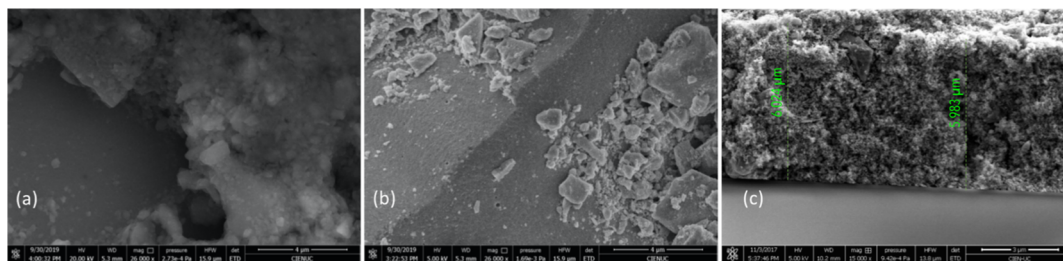
modification of TiO<sub>2</sub> with inorganic compounds such as polyoxometalates (POMs).<sup>16</sup> Among these strategies, fabrication of hybrid materials TiO<sub>2</sub>-POMs has been given great attention due to the photophysical properties of POMs.<sup>17,18</sup> These compounds are metal–oxygen anion nanoclusters formed primarily by the condensation of tungstates or molybdates with or without the involvement of a variety of other elements.<sup>19</sup> Among POMs, there are three main structures, which are known as Keggin, Anderson-Evans, and Wells–Dawson. The Keggin-type structure has a general formula  $X_{n+1}M_{12}O_{40}^{(8-n)}$  ( $M/X = 12$ ); they are the most studied compounds even for catalytic applications, due to their facilities in the synthesis process, relatively high thermal stability, and redox and acidic properties.<sup>20</sup> Knoth et al. reported the first case of Ti-substituted Keggin-type monomeric  $[\text{TiW}_{11}\text{PO}_{40}]^{5-}$  polyoxoanion cluster.<sup>21</sup> The Wells–Dawson-type structure has a general formula of

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**Figure 1.** SEM images: (a) TiO<sub>2</sub> thin films (×26,000), (b) TiO<sub>2</sub>-ALPOM (×26,000), and (c) cross-section SEM ×15,000 image of the TiO<sub>2</sub> films.

X<sub>2n</sub>M<sub>18</sub>O<sub>62</sub><sup>(2n-16)</sup> (X is P<sup>5+</sup>, S<sup>6+</sup>, and As<sup>5+</sup>; M can be W<sup>6+</sup> or Mo<sup>6+</sup>) (*m/x* = 9). The Wells–Dawson-type POMs have reported photocatalytic activity; Fan et al. reported the efficient photocatalytic degradation of different dyes on (P<sub>2</sub>W<sub>18</sub>) modified by a Ag complex.<sup>22</sup> The Anderson-type POMs have a general formula of H<sub>i</sub>(XO<sub>6</sub>)M<sub>18</sub><sup>(n-)</sup> (M/X = 6); they have a plane structure consisting of a central XO<sub>6</sub> octahedral structural unit surrounded by six edge-sharing MO<sub>6</sub> octahedral structural units; these compounds have a great variety of the central heteroatom, which has significant impacts on their electronic and catalytic properties.<sup>23</sup> Qin et al. reported the photocatalytic activity of organic–inorganic hybrid Anderson-type POMs under visible-light irradiation.<sup>24</sup> Wang et al. synthesized novel Anderson-type POMs based on metal–organic frameworks.<sup>25</sup> Because POMs can act as mediators in the dynamics of photocatalytic electronic transfer from the conduction band of TiO<sub>2</sub>, they can be used to form composites with other semiconductors.<sup>26</sup> Diaz-Urbe et al. reported the synergic effect of Anderson-type Cr-POM and Zn-POM anchored to TiO<sub>2</sub> thin films in photocatalytic degradation of methylene blue (MB).<sup>27</sup> Recently, our research group reported the synergic effect of Anderson-type (ZnPOM and CuPOM) and a porphyrin anchored to TiO<sub>2</sub> thin films in photocatalytic degradation of MB.<sup>28</sup>

In this article, we modified TiO<sub>2</sub> thin films with Anderson-type POM aluminum and studied physical adsorption and photocatalytic degradation of MB under UV irradiation. Finally, by means of DFT modeling, the comparison with the previously reported POMs supported over TiO<sub>2</sub> was made, showing a reasonable explanation of the performance observed for the ALPOM reported herein.

## 2. EXPERIMENTAL SECTION

**2.1. Synthesis of the Catalysts and Thin Film Deposition.** The aluminum Anderson-POMs were synthesized as ammoniacal salts with general chemical formula (NH<sub>4</sub>)<sub>3</sub>[AlMo<sub>6</sub>O<sub>24</sub>H<sub>6</sub>]<sup>-3</sup>·4H<sub>2</sub>O. The POM was prepared through the precipitation reaction between the precursor (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (Merck, 99%) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck, ≥99) according to procedure reported by Lee.<sup>29</sup> The synthesized POMs correspond to (NH<sub>4</sub>)<sub>3</sub>[AlMo<sub>6</sub>O<sub>24</sub>H<sub>6</sub>]<sup>-3</sup>·4H<sub>2</sub>O called ALPOM. The TiO<sub>2</sub> films were deposited on soda lime glass by the Doctor Blade method, and TiO<sub>2</sub>–Degussa powder (P25) was used as reagent; the details of the procedure are provided in a previous report.<sup>30,31</sup> The TiO<sub>2</sub> thin films were immersed in a solution of POMs (10 mg/L) for 24 h at room temperature and under constant stirring. Finally, the films were washed with water and dried at 90 °C during 12 h.

**2.2. Characterization of the Thin Films.** The thin films' optical properties were determined by diffuse reflectance using

a Lambda 4 PerkinElmer spectrometer equipped with an integrating sphere. Morphology and elemental surface assays were carried out by scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM–EDX), and the samples were analyzed using the SEM instrument model QUANTA FEG 650 with operation at an acceleration potential of 25.0 kV. For chemical content assay, we used detector EDAX APOLO 126.1 eV (Mn Kα) and the software EDX Genesis to generate the semi-quantitative information.

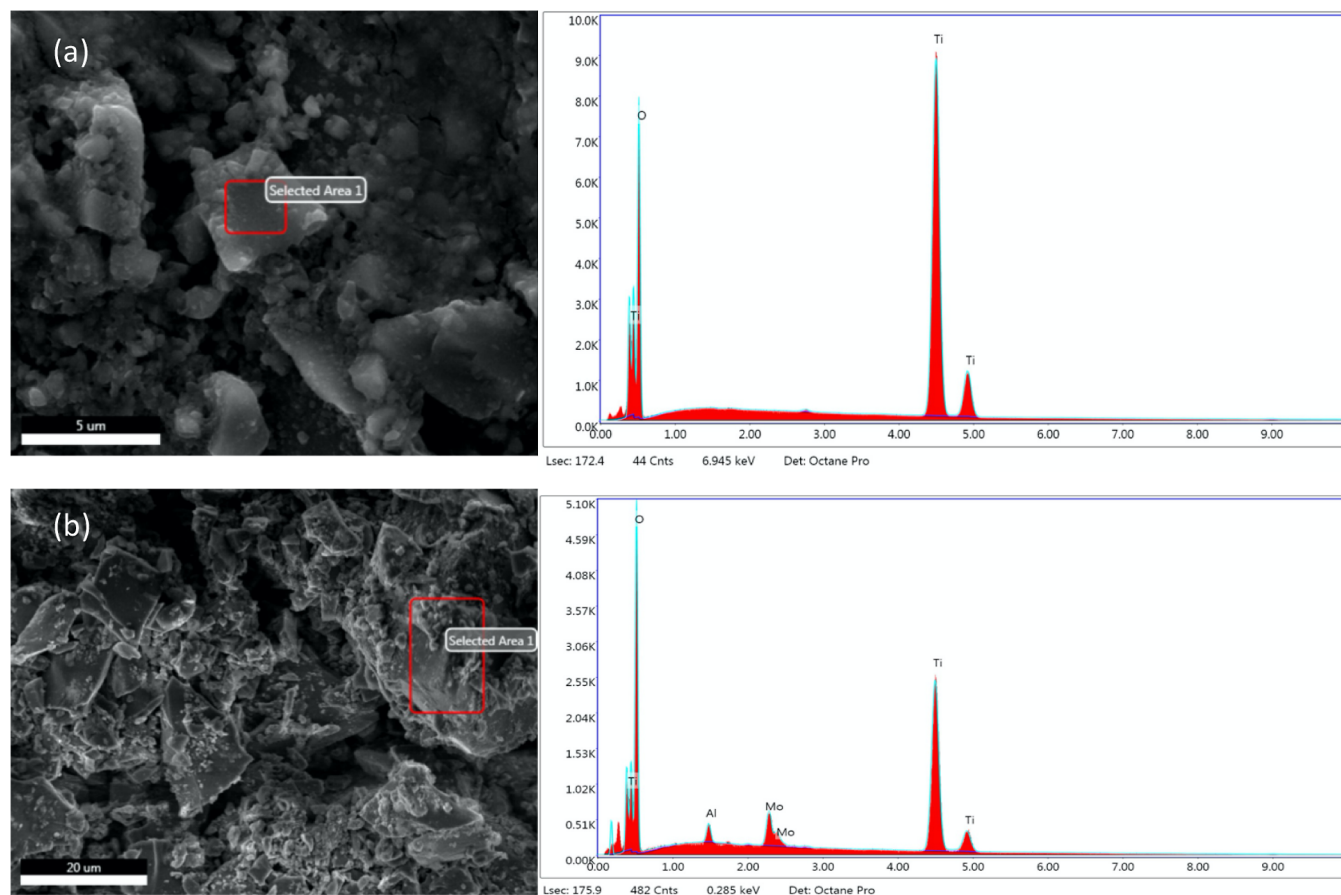
**2.3. Adsorption Study.** We study the kinetic and isothermal adsorption of MB on the thin films fabricated in this work. First, the thin films were immersed in a solution of MB (100 mL; 10 mg/L) (Merck, ≥95%) contained in a batch glass reactor provided with an air bubbling system (0.5 L/min). The reactor was stored in the dark to study the MB adsorption process on the films. An aliquot was extracted at time zero and every 5 min thereafter to track the kinetics of the process and to determine the adsorption–desorption equilibrium time. The process was repeated with different MB concentrations (20, 30, 40, 50, and 60 mg/L). The MB concentration of each aliquot was determined by spectrophotometry at 665 nm (Thermo Scientific Evolution 220 spectrophotometer) using the Lambert–Beer law with a calibration curve (*R*<sup>2</sup> = 0.996). As a previous step to the photocatalytic degradation, the adsorption of contaminant species on the surface of the photocatalyst (sorption/desorption equilibrium) is a very important step of the process; however, this step is not commonly reported in photocatalytic studies. In this work, we studied the adsorption behavior of MB onto both materials fabricated as a previous step to the photocatalytic degradation by using Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isothermal models. All the details of this section are given in [Supporting Information](#) (Section S1).

**2.4. Photocatalytic Study.** Once the adsorption–desorption equilibrium was reached, the reactor with the MB solution (100 mL; 10 mg/L) and the film was irradiated with an UV tubular lamp manufactured by PHILIPS (arc length 161 mm, tube diameter 16 mm, 7 W, 15 μW/cm<sup>2</sup> at 1 m, emission maximum of 260 nm) during 5 h, and every 20 min a sample was extracted to monitor the MB degradation. In the study, the photocatalytic degradation of MB under UV and vis irradiation was fitted with Langmuir–Hinshelwood according to<sup>32</sup>

$$[\text{MB}]_t = [\text{MB}]_0 e^{-k_{\text{ap}}(t)} \quad (1)$$

where  $[\text{MB}]_t$  is the MB concentration as function of light irradiation, (*t*) is the irradiation time, and  $k_{\text{ap}}$  is the apparent reaction rate constant (min<sup>-1</sup>).

**2.5. DFT Study.** Density functional theory (DFT) calculations were carried out with the Amsterdam Density Functional package (ADF 2019.01)<sup>33</sup> at the relativistic level



**Figure 2.** EDX images: (a)  $\text{TiO}_2$  thin films ( $\times 26,000$ ) and (b)  $\text{TiO}_2$ -ALPOM ( $\times 26,000$ ).

including the zeroth order regular approximation Hamiltonian with the scalar corrections.<sup>33,34</sup> Single polarized uncontracted type IV basis sets using triple- $\zeta$  accuracy sets of Slater type orbitals were employed.<sup>35</sup> The generalized gradient approximation method was used for the optimizations via analytical energy gradient techniques using the nonlocal exchange and correlation corrections within the PBE functional.<sup>36</sup> Solvent effects were included using COSMO with water as solvent.<sup>37</sup> Using the bonding energy decomposition analysis, proposed by Morokuma–Ziegler,<sup>33,38,39</sup> the interaction energy,  $\Delta E_{\text{int}}$  was dissected into the  $\Delta E_{\text{elec.}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$  components. (i)  $\Delta E_{\text{elec.}}$  is the electrostatic component, calculated by superposition of the unperturbed fragment densities of the molecular geometry, corresponding to the classical electrostatic effects due to the attractive and repulsive forces; (ii)  $\Delta E_{\text{Pauli}}$  represents the repulsive interactions between the fragments because two electrons with the same spin cannot occupy the same region in the space; and (iii)  $\Delta E_{\text{orb}}$  is the stabilizing orbital interaction term.<sup>40</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Morphological Characterization.** Figure 1 shows the SEM image for  $\text{TiO}_2$  and  $\text{TiO}_2$ -ALPOM thin films. Images show agglomeration in the form of particles on the  $\text{TiO}_2$  thin films with varying sizes. Holes on the  $\text{TiO}_2$  film could be observed; this result could be attributed to the process of homogenization of the catalyst slurry during the Doctor Blade deposition of the films.<sup>41</sup>

The semiconductor industry has developed different methods for thin film depositions (e.g., chemical vapor

deposition, sputtering, thermal evaporation, atomic layer deposition, sol–gel, chemical bath deposition, and Doctor Blade).<sup>42</sup> Among the physical and chemical methods of thin film deposition, the Doctor Blade process is inexpensive and technically suitable one (e.g., temperature and pressure requirements).<sup>43</sup> The Doctor Blade technique deposits thicker films by increasing deposition speed affecting final morphological properties of the coatings.<sup>44</sup>  $\text{TiO}_2$ -ALPOM film has a more heterogeneous surface in terms of particle size and distribution compared with  $\text{TiO}_2$  thin films. This behavior is according to previous reports about  $\text{TiO}_2$  surface modification with POMs. Sun et al. reported particulate aggregation of POMs after electrodeposition of  $\text{PW}^{12}$  polyanions on the  $\text{TiO}_2$  surface.<sup>45</sup> Figure 1c shows the cross-section SEM  $\times 15,000$  image of the  $\text{TiO}_2$  film; the SEM images indicate that the thickness of the  $\text{TiO}_2$  thin films was near  $\sim 6.0 \mu\text{m}$  (average 6 points). Figure 2 shows the EDX assay for  $\text{TiO}_2$  and  $\text{TiO}_2$ -ALPOM thin films, and Table 1 lists the elemental composition of the thin films.

**Table 1. Elemental Composition Analysis for  $\text{TiO}_2$  and  $\text{TiO}_2$ -ALPOM Thin Films**

film <sup>a</sup>	% Ti	% O	% Mo	% Al
$\text{TiO}_2$	33.32	66.68		
$\text{TiO}_2$ -ALPOM	31.53	66.06	2.05	0.36

<sup>a</sup>The film composition was obtained with EDX characterization results.

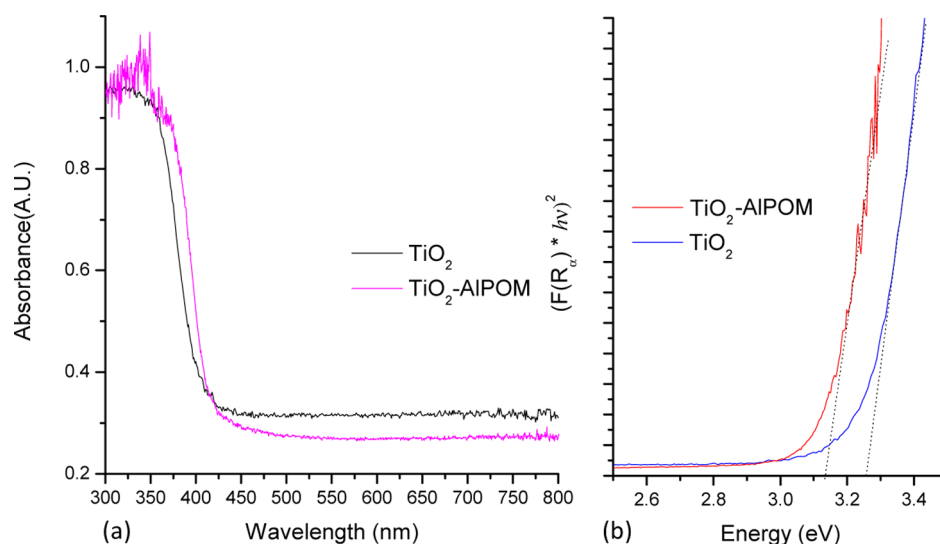


Figure 3. (a) Thin film diffuse reflectance spectra and (b) Kubelka–Munk plots.

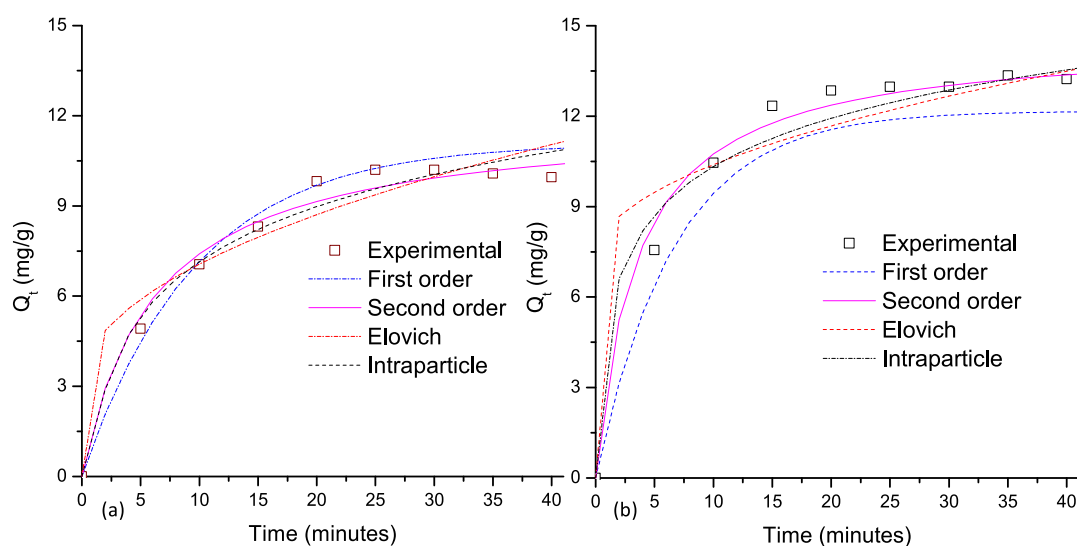


Figure 4. Kinetic results and model fitting for adsorption of MB on: (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2$ -ALPOM thin films.

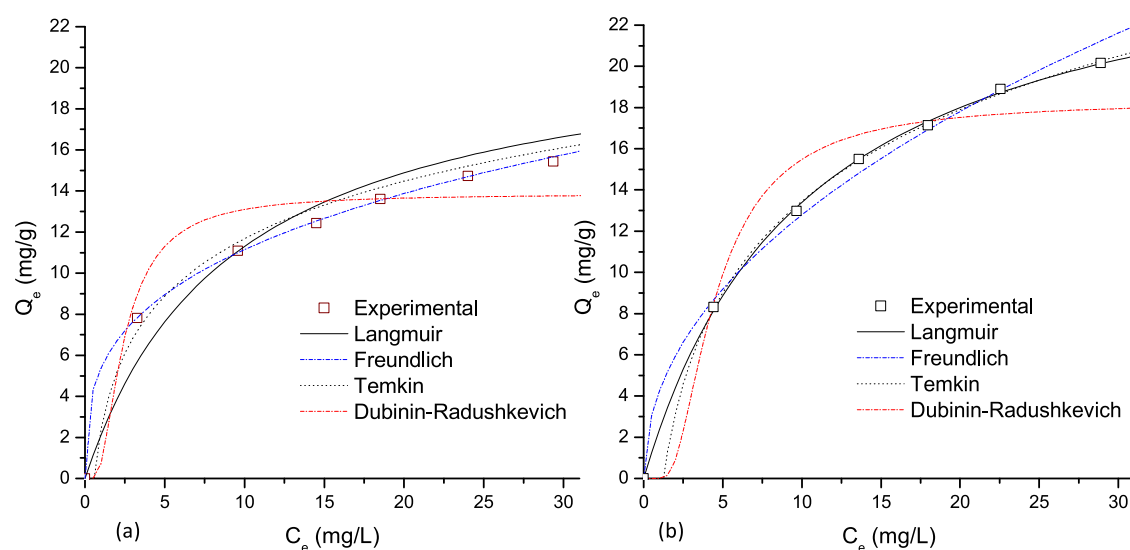
Table 2. Kinetic Values Calculated for MB Sorption Onto Films

thin film/model <sup>a</sup>	1st order	2nd order	Elovich	intraparticle
$\text{TiO}_2$	$qe(\text{mg g}^{-1}) = 11.1$ $k_1 (\text{min}^{-1}) \times 10^{-3} = 104$ $R^2 = 0.960$ ARE (%) = 4.1	$qe(\text{mg/g}) = 11.9$ $K_2 (\text{g mg}^{-1} \text{min}^{-1}) \times 10^{-3} = 163$ $R^2 = 0.987$ ARE (%) = 3.0	$\alpha (\text{mg g}^{-1} \text{min}^{-1}) \times 10^{-2} = 56.8$ $\beta (\text{g mg}^{-1}) = 2.63$ $R^2 = 0.918$ ARE (%) = 8.5	$C (\text{mg/g}) = 3.1$ $k_{id} (\text{g mg}^{-1} \text{min}^{-1/2}) = 1.3$ $R^2 = 0.830$ ARE (%) = 15.3
$\text{TiO}_2$ -ALPOM	$qe(\text{mg g}^{-1}) = 12.1$ $k_1 (\text{min}^{-1}) \times 10^{-3} = 150$ $R^2 = 0.971$ ARE (%) = 6.7	$qe(\text{mg/g}) = 14.6$ $K_2 (\text{g mg}^{-1} \text{min}^{-1}) \times 10^{-3} = 282$ $R^2 = 0.998$ ARE (%) = 2.3	$\alpha (\text{mg g}^{-1} \text{min}^{-1}) \times 10^{-2} = 376$ $\beta (\text{g mg}^{-1}) = 2.31$ $R^2 = 0.841$ ARE (%) = 7.7	$C (\text{mg/g}) = 7.3$ $k_{id} (\text{g mg}^{-1} \text{min}^{-1/2}) = 0.98$ $R^2 = 0.841$ ARE (%) = 29

<sup>a</sup>Parameters obtained from the fitting data of Figure 4.

**3.2. Optical Characterization.** Figure 3a shows the diffuse reflectance spectra for  $\text{TiO}_2$  and  $\text{TiO}_2$ -ALPOM thin films. The  $\text{TiO}_2$  thin films spectra show strong absorption at wavelength higher than 380 nm; this is according to its band gap value and previous reports about  $\text{TiO}_2$  optical properties. The  $\text{TiO}_2$ -ALPOM thin film spectra show that surface modification affects the optical properties of thin films. Figure 3a shows a red shift of the absorption edge of  $\text{TiO}_2$ -ALPOM

thin films compared to bare  $\text{TiO}_2$ . This result is associated with the charge transfer of the Mo(VI) in an octahedral environment. In these structures, the Mo atoms have the highest oxidation state, and Mo(VI) with an electronic configuration  $d_0$  and the ligand to metal charge transfer (LMCT)  $\text{O} \rightarrow \text{Mo}$  could be present.<sup>46</sup> The interaction of the  $\text{TiO}_2$  electronic bands with the POM HOMO–LUMO orbitals allow POMs to act as electron acceptors reducing electron-hole recombination



**Figure 5.** Isothermal results and model fitting for adsorption of MB on: (a)  $\text{TiO}_2$ . (b)  $\text{TiO}_2$ -ALPOM thin films.

**Table 3. Isotherm Models Fitting Results for MB Isotherm Adsorption on Catalysts**

thin film/model <sup>a</sup>	Freundlich	Langmuir	Temkin	Dubinin–Radushkevich
$\text{TiO}_2$	$K_F (\text{mg/g})/(\text{mg/L})^n = 5.4$ $1/n = 0.312$ $R^2 = 0.999$ ARE (%) = 1.0	$q_m (\text{mg/g}) = 21.8$ $K_L (\text{L/mg}) = 0.109$ $R^2 = 0.986$ ARE (%) = 7.5	$B_T = 42.48$ $A_T = 2.40$ $R^2 = 0.918$ ARE (%) = 3.8	$\beta (\text{mol}^2 \text{kJ}^{-2}) \times 10^{-6} = 1.0$ $q_m (\text{mg/g}) = 13.6$ $R^2 = 0.873$ ARE (%) = 10.8
$\text{TiO}_2$ -ALPOM	$K_F (\text{mg/g})/(\text{mg/L})^n = 4.3$ $1/n = 0.477$ $R^2 = 0.986$ ARE (%) = 3.0	$q_m (\text{mg/g}) = 27.4$ $K_L (\text{L/mg}) = 0.100$ $R^2 = 0.999$ ARE (%) = 1.1	$B_T = 6.41$ $A_T = 1.22$ $R^2 = 0.996$ ARE (%) = 1.7	$\beta (\text{mol}^2 \text{kJ}^{-2}) \times 10^{-6} = 3.0$ $q_m (\text{mg/g}) = 18.3$ $R^2 = 0.910$ ARE (%) = 7.9

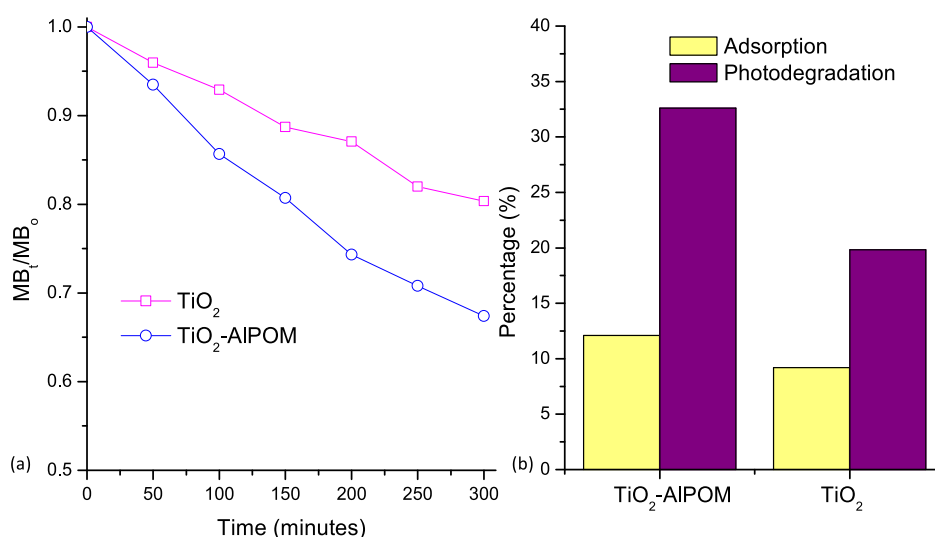
<sup>a</sup>Parameters obtained from the fitting data of Figure 5.

of photo-generated electrons by  $\text{TiO}_2$ .<sup>19</sup> Guo et al., deposited Keggin-type POMs on mesoporous- $\text{TiO}_2$  nanoparticles for photocatalytic degradation of methyl orange.<sup>47</sup> They reported a significant red shift to the visible region UV–vis spectra of the light absorption of  $\text{TiO}_2$  after POM deposition. The band gap energy value was determined using the Kubelka–Munk remission function.<sup>48</sup> Figure 3b shows the plot  $(F(R_\infty)h\nu)^{1/2}$  vs  $(h\nu)$  for the spectra shown in Figure 3a, and Figure 3b shows band gap energy estimation for films. The estimated band gap for materials was 3.24 eV for  $\text{TiO}_2$  thin films and 3.12 eV for  $\text{TiO}_2$ -ALPOM thin films. The  $\text{TiO}_2$  thin films' band gap energy value is in agreement with the reports in literature, which verifies that  $\text{TiO}_2$  is active only under UV irradiation.<sup>49</sup> The change in the optical properties of  $\text{TiO}_2$ -ALPOM thin films is due to the interactions of the  $\text{TiO}_2$  electronic bands with the ALPOM HOMO–LUMO orbitals.<sup>27</sup>

**3.3. Adsorption Study.** **3.3.1. Kinetic Study.** Figure 4 shows the MB adsorption kinetics onto films applying the four theoretical fitting models, and Table 2 shows all the kinetic parameters. The percentage of MB adsorbed on catalysts was 9.96 and 13.1 mg/g for  $\text{TiO}_2$  and  $\text{TiO}_2$ -ALPOM, respectively. The results show an increase in the percentage of MB adsorbed on the surface catalyst after surface modification; this result could be associated to the morphological and ionic nature of POMs: (i) after POM adsorption on the  $\text{TiO}_2$  surface, the surface was more heterogeneous in terms of both particle size and distribution comparing with  $\text{TiO}_2$  thin films (Section 3.1.) affecting the MB adsorption. (ii) The Anderson-type POMs are of an anionic nature, so there is a higher attraction between

the POMs and MB, resulting in a better adsorption on the films.<sup>28</sup> Comparing fitting results (Table 2), the pseudo-second order model showed the best fitting regression values among all models (higher  $R^2$  and lower ARE values). In this model, the effective electrostatic interactions play an important role in adsorption. The results suggest that chemisorption could be the dominant interaction during the adsorption of MB onto both thin films.<sup>32,50</sup>

**3.3.2. Isothermal Study.** Figure 5 shows the isotherm fitting results for MB adsorption on thin films. Table 3 lists the isotherm parameters for all models. According to results listed in Table 3, the Freundlich model was the best fitting model (higher  $R^2$  and smaller ARE) for  $\text{TiO}_2$  thin films. This model is described as a multilayer with a heterogeneous surface. In this model, the adsorption heat and affinities between adsorbent and adsorbates are not uniformly distributed on the heterogeneous surface. Furthermore, this model is commonly utilized in heterogeneous systems (e.g., active carbon, zeolites, and some semiconductors).<sup>51</sup> This model agrees with the morphological results. Furthermore, the Langmuir and Temkin models were the best fitting models for  $\text{TiO}_2$ -ALPOM thin films (ARE and  $R^2$  values are very close for both models). Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). The Temkin model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process.<sup>52</sup> In our case, in heterogeneous surfaces, it is possible that more than one model fits the experimental data, which would mean that several types of adsorption processes



**Figure 6.** (a) MB photocatalytic degradation under UV irradiation onto catalysts. (b) Comparison between TiO<sub>2</sub> and TiO<sub>2</sub>-ALPOM thin films in photocatalytic and adsorption studies.

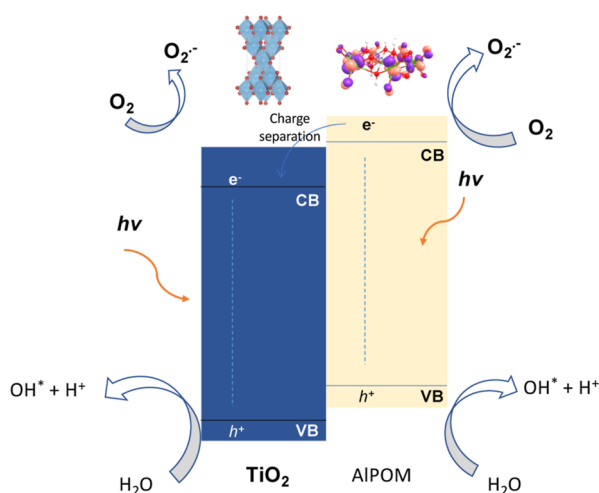
can be present during the adsorption MB on catalysts. This would mean that several types of adsorption processes participate during the MB adsorption process. According to both kinetic and isothermal results, chemisorption could be the dominant interaction during the MB adsorption onto the catalyst, where effective electrostatic interactions play an important role in adsorption.

**3.4. Photocatalytic Study.** Figure 6a shows the MB concentration as a function of UV-irradiation time onto catalysts. The results indicate that TiO<sub>2</sub> thin films reach a 19.6% of MB degradation under UV irradiation and TiO<sub>2</sub>-ALPOM thin films reach a 32.6% MB degradation value. These results are associated with the effect of ALPOM on morphological, optical, and surface properties; besides, the redox properties of POMs can reduce the recombination rates on TiO<sub>2</sub> thin films. The photocatalytic data were fitted using the Langmuir–Hinshelwood model (eq 1). Results indicated that  $k_{ap}$  was  $7 \times 10^{-4} \text{ min}^{-1}$  for TiO<sub>2</sub> and  $13 \times 10^{-4} \text{ min}^{-1}$  for TiO<sub>2</sub>-ALPOM. Comparing these results, the TiO<sub>2</sub>-ALPOM thin films were 1.85 faster than TiO<sub>2</sub> thin films in MB photodegradation. After modification, POMs can act as a scavenger, gathering photogenerated electrons from the TiO<sub>2</sub> and delaying the recombination of charge carriers.<sup>19,53</sup> The ALPOM interaction with TiO<sub>2</sub> changes morphological, optical, and adsorption catalyst properties, generating a synergic effect in the photocatalytic activity. Comparing the herein obtained results with previous reports,  $k_{ap}$  for TiO<sub>2</sub>-ALPOM is smaller than the  $k_{ap}$  value reported for TiO<sub>2</sub> thin films modified with Cr-POM ( $60 \times 10^{-3} \text{ min}^{-1}$ ).<sup>54</sup> In this case, the electronic configuration of Al inside the POM does not possess free “d” orbital compared with Cr that has free “d” orbital to reduce recombination rates. Figure 6b shows the comparison between TiO<sub>2</sub> and TiO<sub>2</sub>-ALPOM thin films in photocatalytic and adsorption studies.

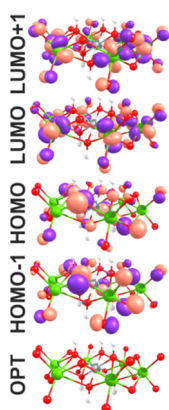
The comparative study showed that TiO<sub>2</sub> thin films reach a 19.6% MB degradation under UV irradiation and 9.1% MB adsorption, while the TiO<sub>2</sub>-ALPOM thin films reach a 32.6% MB degradation and 12.1% MB adsorption on their surface. In combination (adsorption and photodegradation), TiO<sub>2</sub> thin films reach 27.1% MB removal and TiO<sub>2</sub>-ALPOM thin films reach 44.6% MB removal. The previous stage to the

photocatalytic degradation is more efficient to anchor more MB on the catalyst surface to TiO<sub>2</sub>-ALPOM than to TiO<sub>2</sub> thin films, which is due to anionic properties of the POM. Furthermore, POMs can be photocatalytic active under UV irradiation, which could make the POM a generator of reactive species contributing to the degradation of the model pollutant.<sup>55</sup> POMs have an electronic structure similar to the semiconductors (e.g., conduction band and valence band).<sup>23,53</sup> Figure S1 shows the UV–vis absorption spectra of ALPOM in an aqueous solution. Figure S1 shows two absorption bands close to 208 and 228 nm; the transitions are associated with ligand to metal charge transfer (O → Mo); these charge transfers have been reported at wavelengths between 200 and 350 nm.<sup>46</sup> This photoexcitation of the POMs can be applied in HP.<sup>56</sup> In our case, the composite structure TiO<sub>2</sub>-ALPOM improved the photocatalytic yield compared with the bare TiO<sub>2</sub> thin films due to three reasons: (i) ALPOM can generate reactive oxygen species (ROS) in the same way that TiO<sub>2</sub> can, which increases the charge carriers available to photodegradation; (ii) the heterostructure of composite TiO<sub>2</sub>-ALPOM assists the charge separation, reducing the recombination process; and (iii) the surface area of the semiconductor can increase after POM modification.<sup>19,57</sup> After charge pairs generation (by TiO<sub>2</sub> and/or ALPOM), the ROS can be yielded on the composite surface and MB degradation starts. Figure 7 shows the ROS process for TiO<sub>2</sub>-ALPOM thin films.

**3.5. DFT Study.** There is a previous study on the POM family with Co, Cr, and Ni. It was shown that the best catalyst for the photocatalytic MB degradation among those three compounds adsorbed over TiO<sub>2</sub> was Cr.<sup>54</sup> This was due to the presence of unpaired electrons due to the oxidation state of the central metallic atom. Furthermore, it was shown that the more spin density is located over the central metallic atom, the better the catalyst is. This situation was outstanding for the Cr-POM, which showed the large unpaired spin between all the former studied derivatives. Thus, when there is a large participation of the surrounding metallic atoms, the catalyst is worse. In this report, as can be observed in Figure 8, the geometry of the POM does not get affected by the inclusion of the Al<sup>3+</sup> at the center of the POM. The Frontier molecular orbitals (FMO) are mostly located over the surrounding atoms of the Anderson



**Figure 7.** (a) Photocatalytic scheme of TiO<sub>2</sub>-ALPOM thin films fabricated in this work. Inset: CB is the conduction band and VB is the valence band.



**Figure 8.** FMOs for ALPOM synthesized.

POM. Furthermore, there is no spin density, as the Al<sup>3+</sup> corresponds to a close shell atom, which does not show any unpaired electrons. In terms of stabilization energy, the reported compound does show a stability similar to the best catalyst reported before (−92.4 eV). This stability can be related to the long-lasting stability of the studied molecule in the reaction procedure. Finally, 71% of the observed stabilization energy corresponds to electrostatic interaction inside the molecule and between the central metallic (−69.1 eV) Al<sup>3+</sup> atom and the surrounding structure, whereas the orbital energy represents only 29% (−28.2 eV). This observation is similar to the previous report.

#### 4. CONCLUSIONS

In this work, we modified TiO<sub>2</sub> thin films with ALPOM. The catalysts were characterized by optical and morphological techniques. We studied the effect of ALPOM on TiO<sub>2</sub> thin films properties for adsorption and photocatalytic degradation of MB. After ALPOM modification, the thin films' adsorption capacity and photocatalytic activity improved. These results were associated with a synergic effect between Al-POM and TiO<sub>2</sub>. After POM modification, the adsorption capacity changed from 9.1 to 12.2%, and the photocatalytic efficiency changed from 19.6 to 32.6%; the best results were obtained using TiO<sub>2</sub>-ALPOM thin films. Results show that several types

of adsorption processes participate during the MB adsorption process, and results indicated that the adsorption process is an important step prior to photocatalytic degradation (remove an important amount of the pollutant). Furthermore, the TiO<sub>2</sub>-ALPOM thin films were 1.85 faster than TiO<sub>2</sub> thin films in MB photodegradation. DFT results showed that the geometry of the POM does not get affected by the inclusion of the Al<sup>3+</sup> at the center of the POM generating long-lasting stability for adsorption and photocatalytic application.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c02657>.

Isothermal and kinetic models and UV–vis absorption spectra of synthesized ALPOM (PDF)

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##### Notes

The authors declare no competing financial interest.

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